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Synthesis of poly[(styrene)-*rotaxa*-(crown ether)]s via free radical polymerization

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Abstract

Poly[(styrene)-*rotaxa*-(crown ether)]s were synthesized by free radical polymerizations of styrene in the presence of crown ethers using bulky 'blocking group' initiators to ensure end-capping for prevention of dethreading. These statistical processes produced only low threading yields, but up to 26% cyclic by mass with large crown ethers. The poly[(styrene)-*rotaxa*-(crown ether)]s 'emulsified' in protic solvents such as methanol and water. The dispersion polymerization of styrene in methanol or water using '42-crown-14' ('42C14') indicated that threading provided stability of the polyrotaxane micelles in such solvents through hydrophilic–hydrophobic phase separation. DSC investigations indicated that the threading prevents the crystallization of the crown ether and allows phase mixing to some extent, since two altered T_g's were observed.

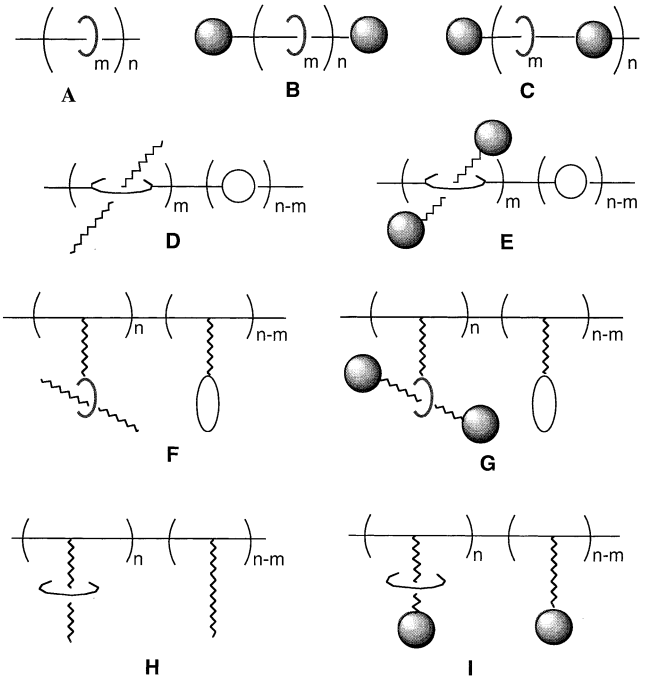
Keywords: Polyrotaxanes; Crown ethers; Micelles

1. Introduction

By incorporation of different linear and cyclic components into polyrotaxanes (Scheme 1) [1–4], in which rotaxane structures are incorporated into macromolecules, new combinations of material properties can be achieved.

The two major approaches for polyrotaxane syntheses are polymerization of monomers in the presence of cyclic species and direct mixing of linear and cyclic component molecules (Scheme 2). The latter include charge transfer driven threading of bipyridinum macromolecules onto electron rich backbones [5,6] or bisphenylene crown ethers onto polymers containing bipyridinum units [7,8] or bipyridinium ions into macrocycles that are part of macromolecular structures [8–10]. We have employed hydrogen bonding to thread crown ethers onto a preformed polyurethane in the melt and solution states [11]. Poly(ethylene oxide)s [12], poly(propylene oxide)s [12], polyisobutylene [13] or polyammonium ions [14,15] when mixed with cyclodextrins (CDs) in aqueous phases give highly threaded polyrotaxanes, driven by hydrophobic–hydrophilic interactions between the two components [16–18].

The more versatile methodology of polyrotaxane



Scheme 1. Various types of polyrotaxanes, including main chain (A–E) and side chain (F–I) systems. Systems without blocking groups (A, D, F, H) are 'pseudorotaxanes' while those with such blocking groups (B, C, E, G, I) are true rotaxanes.

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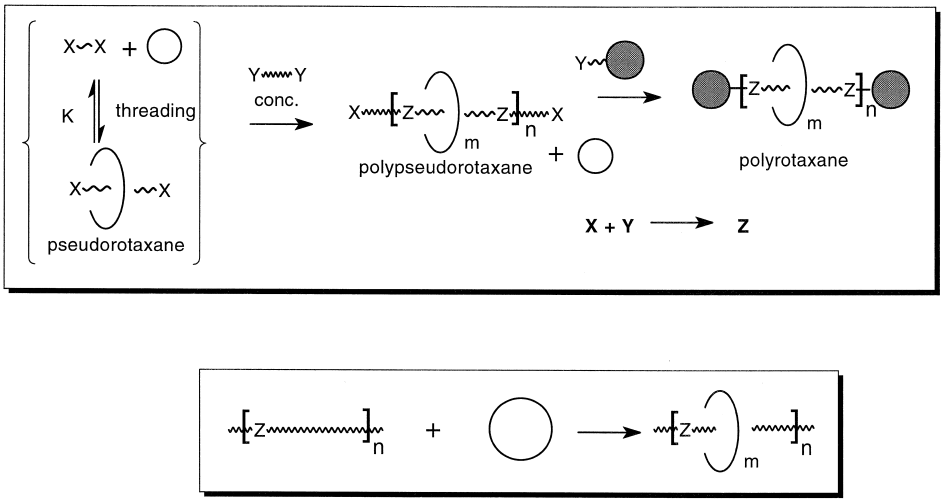


Scheme 2. Methods of synthesis of main chain polyrotaxanes of Types A and B: (a) by polymerization in the presence of macrocycle, (b) by threading macrocycles onto a preformed polymer.

synthesis is the in situ polymerization of monomers in the presence of macrocycles. By this method, it is possible to prepare polyrotaxanes with various types of backbones and macrocycles. The threading yields or the degrees of loading of the macrocyles in the final polyrotaxanes depend on the strength of the attractive forces between the two components, such as hydrophilic–hydrophobic effects with CDs [19], H-bonding [20–33] or charge transfer interactions with crown ethers [7,34]. We have successfully demonstrated this methodology in the preparation of polyrotaxanes by step growth polymerizations of various monomers to yield traditional linear backbones such as polyamides [20], polyurethanes [7,21–25,34] and polyesters [26–33] using crown ethers as cyclic species, as well as by chemical modification of a polymethacrylate [35].

In the literature there are only a few reports on the synthesis of polyrotaxanes via free radical polymerizations. Maciejewski and coworkers carried out free radical polymerizations of various monomers including vinylidene chloride [36–38], styrene and methacrylonitrile [37,38] in the presence of β-CD in DMF solution using AIBN as an initiator. According to the reports, they obtained poly(vinylidene chloride) rotaxanes with up to 70 wt% threaded β-CD [36–38]. Lipatova et al. synthesized polystyrene (PS) rotaxanes containing up to 40 vol% of a 34-membered cyclic urethane by thermal polymerization of styrene at room temperature over 3–5 months in the presence of the macrocycle [39,40]. The polyrotaxanes were reported to show unique properties, including solubilities and crystal structures which were different from the original components. We reported the synthesis of polyacrylonitrile-based rotaxanes [41].

Here we report the free radical synthesis and characterization of poly[(styrene)-*rotaxa*-(crown ether)]s, a new system.

2. Experimental section

2.1. Experimental methods and measurements

NMR spectra were obtained on Bruker 200 or 270 Mhz or Varian 400 MHz spectrometers at ambient temperature using Me_4Si as an internal standard. Centrifugation was done at 6000–7000 rpm. GPC analyses of the polymers were performed at 20°C in THF or $CHCl_3$ using two Waters systems, one with refractive index and UV detectors calibrated with PS standards, and one with u.v. and Viscotek 100 differential viscometer detectors using the universal calibration; the traces shown in the various figures correspond to different columns at different times and are not directly comparable. Thermal analyses were done on Perkin Elmer DSC-7 or TA Instruments DSC 2920 machines at 10°C/min.

2.2. Synthesis of poly[(styrene)-*rotaxa*-(crown ether)]s **7** (**7**c, Sample L261 as typical) via free radical polymerization

A solution of styrene (0.50 g, 4.8 mmol), '42c14' [42] (**5**, 2.0 g), **2** [43] (60 mg, 4.8×10^{-5} mol) and toluene (2.0 g) was subjected to three cycles of freeze–pump–thaw processes on a vacuum line (1×10^{-5} Torr) and stirred by a magnetic stirrer in a pre-heated oil bath at 90–95°C for 3 days. To the mixture, CH_2Cl_2 (ca. 5 ml) was added and the solution was poured into MeOH (250 ml) with vigorous stirring. An emulsion formed and it was filtered with a very fine sintered glass filter. To the precipitate, EtOH (50 ml) was added and the mixture was stirred using a magnetic stirrer. The precipitate turned back to an emulsion, which was subjected to centrifugation for ca. 2 h. The supernatant liquid was decanted and EtOH (50 ml) was added to the precipitate. The same procedure (stirring, centrifugation

Table 1
Synthesis of polystyrene (**7**, $m = 0$) and poly[(styrene)-rotaxa-(crown ether)]s **7a**–**7c** by free radical polymerization.

Sample	Styrene (mmol)	Cyclic (mmol)	Solvent[a] (ml)	Init. (mol%)	T/t (°C/h)	Yield (%)	M_n (kg/mol)	PDI	$n/10$	$(n/10m)$[b]	Mass % crown
E133	4.3	**3**/1.9	—	**1**/1.0	100/20	33[c]	16.4[d]	1.58[d]	16	∞	0
E136-1	4.3	**3**/0.93	T/0.5	**1**/1.0	100/20	54[c]	9.6[d]	2.83[d]	9.2	14	3.0
E136-2	4.3	**3**/0.93	T/1.0	**1**/1.0	100/20	54[c]	12.4[d]	2.23[d]	12	17	3.5
E125-1	4.4	—	T/1.0	**2**/1.3	100/20	70[e]	15.1[d]	1.92[d]	15	∞	0
E128-3	4.4	—	M/1.0	**2**/1.3	100/20	53[e]	14.8[d]	1.72[d]	14	∞	0
E125-2	4.4	—	T/1.0	**2**/2.5	100/20	63[e]	10.5[d]	1.49[d]	10	∞	0
E128-4	4.4	—	M/1.0	**2**/2.5	100/20	46[e]	10.7[d]	1.60[d]	10	∞	0
L239	4.3	**4**/4.5	T/2.0	**2**/1.0	90/72	87[c]	27.7[f]	2.47[f]	27	30	1.4
L195-5	4.8	**6**/7.6	T/2.0	**2**/1.0	90/72	90[e]	—	—	—	130	0.2
L261	4.8	**5**[g]/3.2[h]	T/2.0	**2**/1.0	90/72	36[i]	23.4[f]	1.28[f]	23	2.2[h]	21
E216-3	13.5	**5**[g]/3.2[h]	B/1.0	**2**/5.0	60/72	60[i]	49.3[j]	3.81[j]	49	13[h]	2.6
E216-4	13.5	—	B/1.0	**2**/5.0	60/72	60[i]	26.9[j]	3.41[j]	27	∞	0
E210-3	19.5	**5**[g]/4.9[h]	B/1.0	A[k]/0.5	55/72	72[l]	23.8[j]	2.35[j]	24	4.4[h]	12
101-2	5.0	**5**[g]/2.0[h]	T/2.0	**2**/1.0	90/72	8[m]	18.5[n]	3.49[n]	18	4.0[h]	13
L101-3	5.0	**5**[g]/3.2[h]	T/2.0	**2**/1.5	90/72	18[m]	2.6[n]	9.19[n]	2.5	1.7[h]	26
L31-5	5.0	—	T/4.0	**2**/1.0	90/72	59[c]	15.2[n]	1.88[n]	15	∞	0

[a] T = toluene; B = benzene; M = 1:1 molar mixture of *p*-dimethoxybenzene and tri(ethylene glycol) dimethyl ether.
[b] Determined by ^{1}H NMR by integration of OCH_2 signals of the crown ether versus the C_6H_5 signal of PS, estimated error: ± 10%.
[c] Precipitations into methanol (× 3).
[d] Determined by GPC in THF using PS standards.
[e] Precipititation from CH_2Cl_2 into hexanes 2*X*, into MeOH 1*X*.
[f] Determined by GPC in $CHCl_3$ using a viscosity detector and universal calibration.
[g] A mixture of crown ethers with different sizes [42].
[h] Calculated based on the molecular weight = 616.
[i] Precipitation into methanol and filtration followed by centrifugation, 2*X*.
[j] Determined by GPC in THF using a viscosity detector and the universal calibration.
[k] A = AIBN.
[l] Precipitation from CH_2Cl_2 into MeOH, 5*X*.
[m] Purified by silica gel column chromatography by sequential elution with CH_2Cl_2 [**2** + PS (24% for L103-2 and 40% for L103-3)]), then THF (polyrotaxane).
[n] Determined by GPC in $CHCl_3$ with PS standards.

and decantation) was repeated. The precipitate was dried under vacuum at room temperature (RT) to give a white powder (180 mg, 36% yield). GPC: M_n = 23.4 kg/mol, PDI = 1.3 (universal calibration, solvent $CHCl_3$, differential viscometric detector).

2.3. Control experiment: precipitation of a mixture of PS/'42c14' into methanol

A mixture of PS (M_n = 18 K, 0.5 g) and '42c14' (**5**, 2.0 g) was dissolved in CH_2Cl_2 (5 ml) and poured into vigorously stirred MeOH (250 ml). The white precipitate was filtered and dissolved in CH_2Cl_2 (5 ml) and then precipitated into MeOH (250 ml). The precipitate was filtered and dried; the ^{1}H NMR spectrum in $CDCl_3$ showed that the precipitate was PS with no crown ether present.

2.4. Dispersion polymerization of styrene using '42c14' (**5**) as a pre-surfactant (typical procedure)

A 25-ml flask containing styrene (1.5 g, 14 mmol), 4,4′-azobis(4-cyanopentanoic acid) (80 mg, 0.22 mmol), '42c14' [42] (**5**, 1.0 g) and MeOH (10 ml) was placed in a pre-heated oil bath (70°C). After 5–10 min, the mixture became hazy and turned milky after about 30 min. The reaction was continued for 25 h. The resultant emulsion was stable for at least a week.

2.5. Statistical threading of preformed PS with '42c14' (**5**)

Polystyrene (M_n = 18 kg/mol, PDI = 1.2) (0.10 g) and '42c14' (**5**, 1.0 g) were dissolved in THF (6 ml) and the mixture was stirred at reflux for a week. The solution was poured into methanol (50 ml) with vigorous stirring. A white precipitate formed. The filtered precipitate was dissolved in CH_2Cl_2 (3 ml) and reprecipitated into methanol (50 ml). A third reprecipitation was carried out by the same procedure. Precipitation occurred, but the filtrate was not clear; instead, it was an emulsion. The precipitate (0.10 g) was isolated by centrifugation and found to contain 0.3 mass% of crown ether from its ^{1}H NMR spectrum.

3. Results and discussion

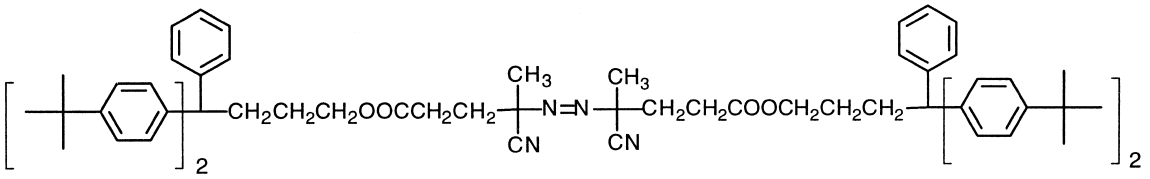
3.1. Synthesis of poly[(styrene)-rotaxa-(crown ether)]s by in situ threading during free radical polymerization

3.1.1. Solution polymerization

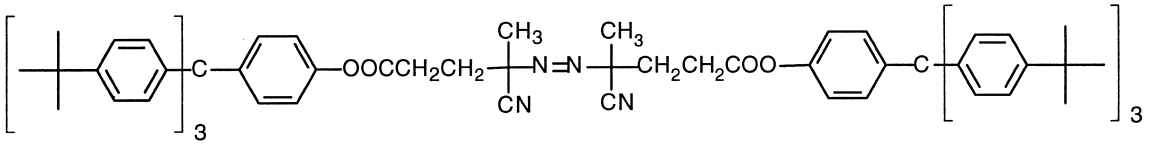
We recently reported syntheses of the blocking group/

initiators (BG/inits) **1** and **2** [43]. These azo initiators contain triarylmethyl moieties to ensure end blocking in free radical polymerizations of styrene, which terminates nearly completely by combination [44–46]; by end group analysis (NMR) and molecular weight determination (GPC) we confirmed that under the current reaction conditions there are two BG's per polystyrene molecule [43]. The *tris*(*p-tert*-butylphenyl)methyl unit, can constrain up to 42-membered rings [47,48]. Using the BG/inits the polymerizations of styrene in the presence of crown ethers [bis(*para*-phenylene)-34-crown-10 (BPP34c10, **3**) [49,50], 30-crown-10 (30c10, **4**) [51] or '42-crown-14' ('42c14', **5**) [42]] gave poly[(styrene)-*rotaxa*-(crown ether)]s **7a**–**7c**. Toluene or benzene was employed as a cosolvent to maintain homogeneity. Table 1 summarizes the results.

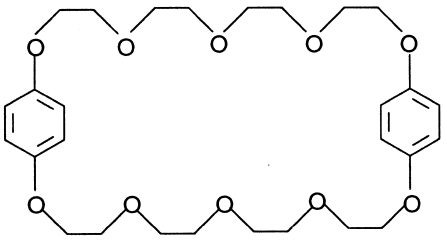
Unthreaded crown ethers were removed by multiple reprecipitations of the samples into excess methanol, which is a good solvent for crown ethers but a non-solvent for PS as demonstrated by the control experiment; when a mixture of PS and '42c14' (**5**) in CH_2Cl_2 was precipitated into methanol twice,

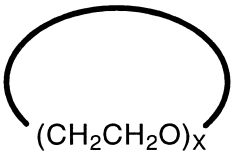


1 (*meso* diastereomer)



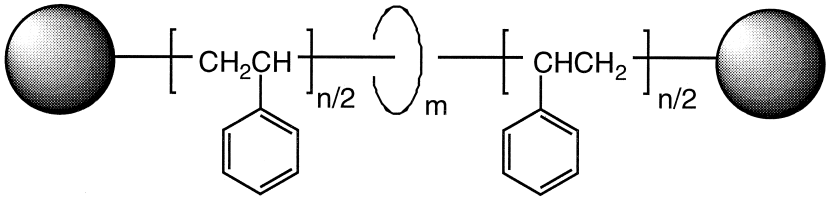
2 (*dl/meso* = 0.78)



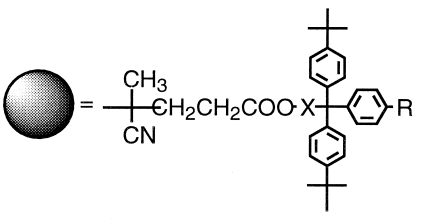


4: x = 10 (30c10)
5: $\overline{x}$ = 54.5 ("42c14")
6: x = 6 (18c6)

3 (BPP)



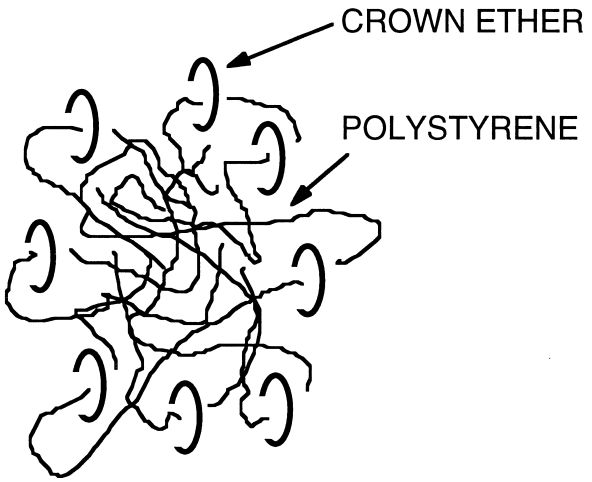
7



a. ○ = **3**, X = $(CH_2)_3$, R = H

b. ○ = **4**, X = *p*-C_6H_4, R = *t*-Bu

c. ○ = **5**, X = *p*-C_6H_4, R = *t*-Bu



the resultant precipitate was homo-PS containing *no* crown ether. The samples of **7** were monitored by ^{1}H NMR spectra for each precipitation step and once the ratio of the peak integrations of the backbone and crown ether reached constant values (e.g., Figs 1 and 2 for **7a** and **7c**, Samples E136-1 and L261), we concluded that the samples did not contain free crown ether. The absence of free macrocycle was demonstrated by GPC (Figs 3 and 4). As shown in Fig. 3(b), a physical blend of PS and '42c14' (**5**) gave two isolated peaks, and thus the trace of **7c** (Fig. 3(c)) indicated that there was no free crown ether

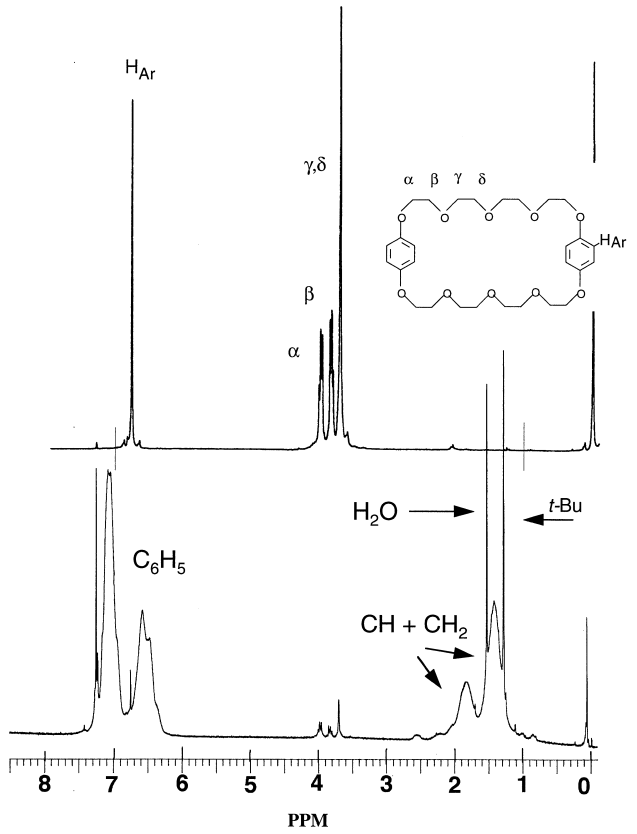


Fig. 1. ^{1}H NMR spectra of (a) bis(*p*-phenylene)-34-crown-10 (**3**) and (b) poly[(styrene)-*rotaxa*-(BPP34c10)] (**7a**, Sample E136-1, Table 1) ($CDCl_3$, 270 MHz).

(Fig. 3(a)) in the product. Similar results were obtained with **7a** (Fig. 4) and **7b**; Fig. 4 shows the clear separation of the low molecular weight crown ether **3** and the polyrotaxane. Crown ethers tail appreciably on silica gel, but with alumina and methanol tailing is absent and mobility is high ($R_f = 0.86$). Polystyrene is immobile under these conditions, but is mobile in CH_2Cl_2 or THF ($R_f = 0.8$). This provides an additional means of establishing the absence of unthreaded crown ether in the purified polyrotaxanes by thin layer chromatography.

The use of a cosolvent was necessary in the syntheses. Without cosolvent the PS precipitated out and there was no threading, as was the case of Sample E-133; the result for Sample E-133 is important, however, because it demonstrates again the efficacy of the purification protocol in removing unthreaded crown ether. As shown with Samples E-136-1 and E-136-2 the degree of threading actually increases somewhat with more solvent up to a point, even though the overall concentrations are reduced; this is due to the fact that phase separation occurred when insufficient amounts of solvent were employed.

The threading yields of the products **7a** and **7b** (Samples E136-1, E136-2 and L239) derived from the 30- and 34-membered crown ethers **4** and **3** on average correspond to less than one cyclic molecule threaded per linear backbone [calculated as equal to $(n/10)/(n/10m)$]. This is due to the lack of attractive interactions between the crown ethers and styrene or PS, i.e., the statistical nature of the threading process.

However, the low m/n values raise the possibility that the incorporation of the crown ethers arises by chain transfer. To address this possibility several experiments were carried out. In the case of BPP34c10 (**3**) we compared the molecular weights of polystyrene prepared in toluene with those prepared in a 1:1 (molar) mixture of *p*-dimethoxybenzene and tri(ethylene glycol) dimethyl ether, 'triglyme', a solvent system designed to mimic BPP34c10 (**3**). The results of these experiments (Table 1, Samples E125-1, E128-3, E125-2 and E128-4), molecular weights in the mixture identical within experimental error to those in toluene, indicate that BPP34c10 undergoes chain transfer to an extent less than or equal to toluene; toluene has a chain transfer constant of 0.105×10^{-4} with polystyryl radical at 60°C, a value less than 5 times that of benzene [52]. An additional set of experiments confirmed that chain transfer was not the mechanism of incorporation of BPP34c10 (**3**). Samples E136-1 and E136-2 incorporated 0.66 and 0.71 BPP34c10 units per macromolecule $[n/(n/m)]$; end group analysis by ^{1}H NMR spectroscopy proved that the numbers of end groups, quantified by the integrals for the *t*-butyl methyl protons, were equal to 2.0 and 1.9 ($\pm$ 0.10), respectively, indicating that within experimental error all the macromolecules were terminated with blocking groups at both ends and not with crown ether moieties. Additionally, a control experiment using 18c6 (**6**), whose cavity size is too small to be threaded [47,48], was also carried out to ensure the absence of chain transfer in the case of the

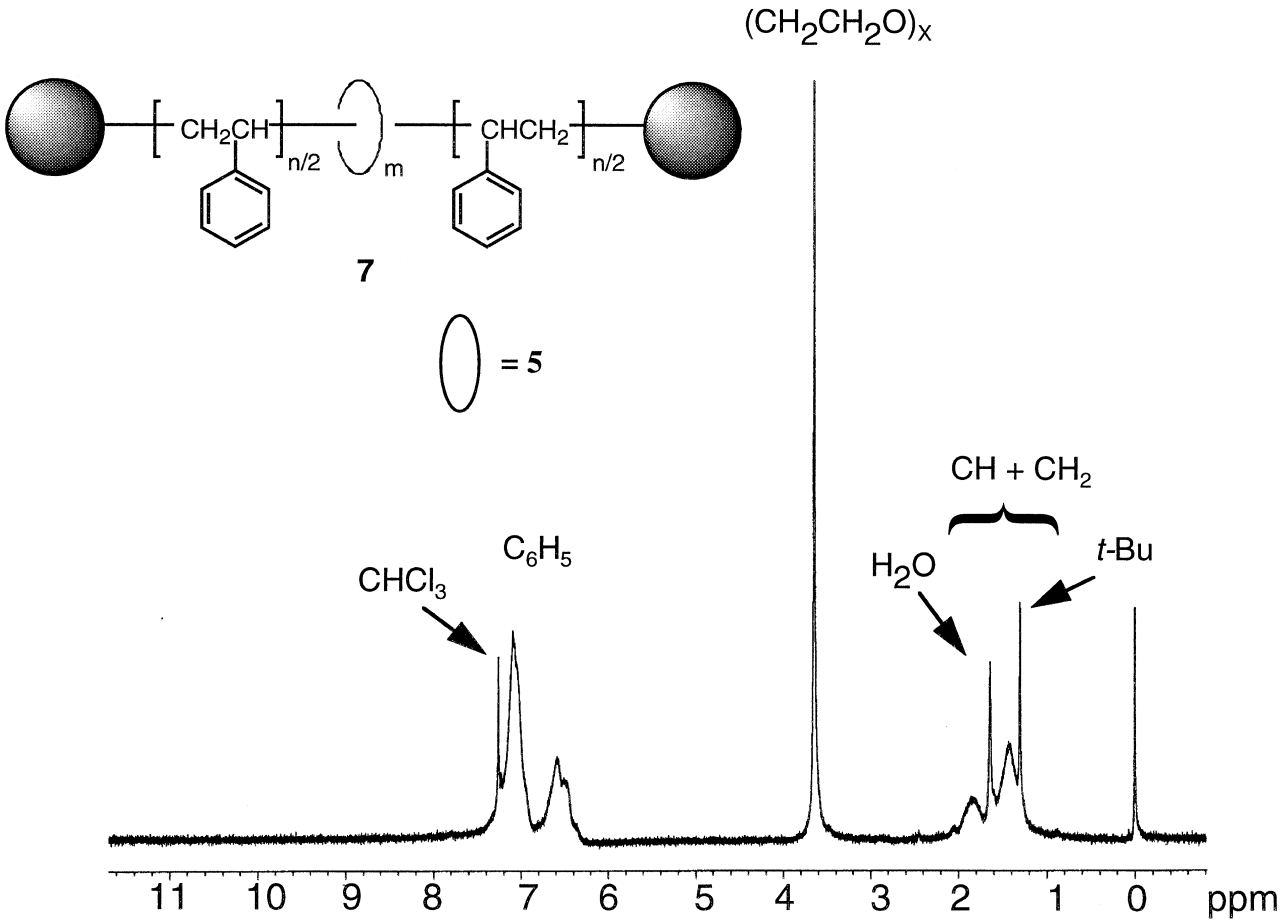


Fig. 2. ^{1}H NMR spectrum of poly[(styrene)-*rotaxa*-('42c14')] (**7c**, Sample L261, Table 1) ($CDCl_3$, 400 MHz).

fully aliphatic crown ethers **4** and **5**. The result for Sample L195-5 indicated that the amount of chain transfer was negligible.

When the larger crown ether **5** was employed, the cyclic loading of **7c** was found to be as high as 26 mass%. The higher threading yields of Samples L261 and L101-3 indicate that in the statistical threading process the cavity size of the cyclic molecule is a major factor governing the threading yield [53].

A characteristic of polyrotaxanes **7** was the capacity to form emulsions in protic solvents such as water or methanol. Due to the emulsification the removal of free crown ether from the crude products was difficult to accomplish. The emulsions which were formed upon pouring the sample into excess methanol easily passed through normal filter paper and glass filters. Centrifugation was used to isolate the polyrotaxane in several cases. The lower yield and PDI of Sample L261 compared to the others was probably due to the loss of more product during the purification steps, i.e., fractionation. It is believed that the particles consisted of a PS-rich inner layer and a crown-rich outer layer in those protic solvents because PS is hydrophobic and the crown ether is hydrophilic. The threading provided the polystyrene with a hydrophilic sheath as hypothesized in cartoon **8**; the crown ethers act as emulsifiers like PEO in PS–PEO block copolymers [54]. See below for a test of this hypothesis. In the case of Sample E216-3, which was prepared with a lower crown ether:styrene ratio at a lower temperature and isolated in higher yield by simple reprecipitation into methanol, a low *m*/*n* value was observed in the resulting **7c**. This result supports the idea that the high threading yield observed with Sample L261 was due to fractionation.

In the case of Samples L101-2 and L101-3, column chromatography on silica gel was used to purify the polyrotaxanes; here frationation on the basis of both molecular weight and crown ether content could occur. This might explain the low molecular weight observed with Sample L101-3. Unthreaded polystyrene and unreacted initiator **2** were exhaustively eluted with CH_2Cl_2 (24 and 40% yields, respectively); then the polyrotaxanes were eluted in low yields (8, 18% respectively) with THF. The fractionated polyrotaxanes were 13 and 26 mass% crown ether, respectively. Subsequent elution with methanol afforded emulsions, presumably containing polyrotaxane **7c** with higher crown ether content and perhaps molecular weight. Sample L101-2 displayed a bimodal GPC trace (Fig. 5); the two peaks probably represent polyrotaxanes with different compositions and/or molecular weights; indeed the apparent M_n

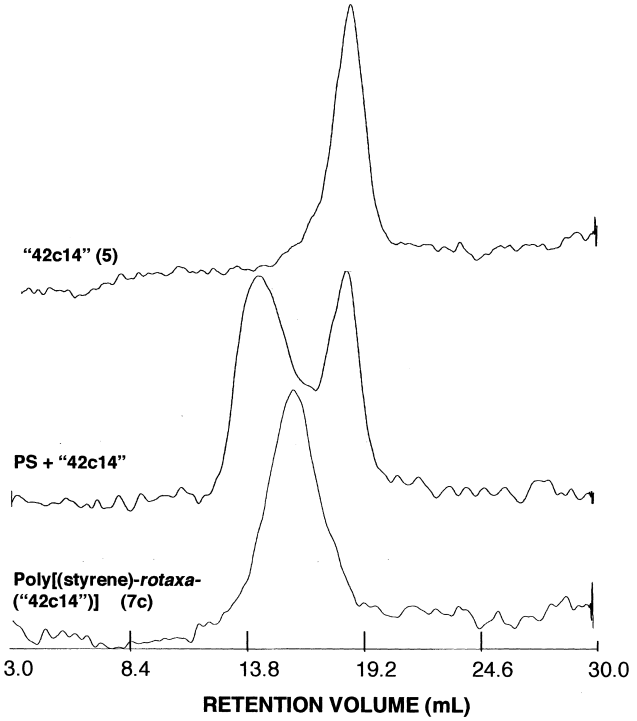


Fig. 3. GPC traces of (a) '42c14' (**5**, M_n = 2.4 kg/mol, PDI = 1.08), (b) a mixture of '42c14' (**5**) and PS (M_n = 35.5 kg/mol, PDI = 2.4), and (c) poly[(styrene)-*rotaxa*-('42c14')] (**7c,** Sample L261, M_n = 23.4 kg/mol, PDI = 1.3): solvent $CHCl_3$, differential viscometric detector, universal calibration.

value based on PS standards was higher than that (M_n = 15 k) of Sample L31-5 prepared under nearly identical concentrations in the absence of the crown ethers. It has been shown that the hydrodynamic volume of polymers is increased by forming rotaxanes [30]. Although all other samples in Table 1 gave monomodal GPC curves, the same molecular weight effect can be seen by comparison

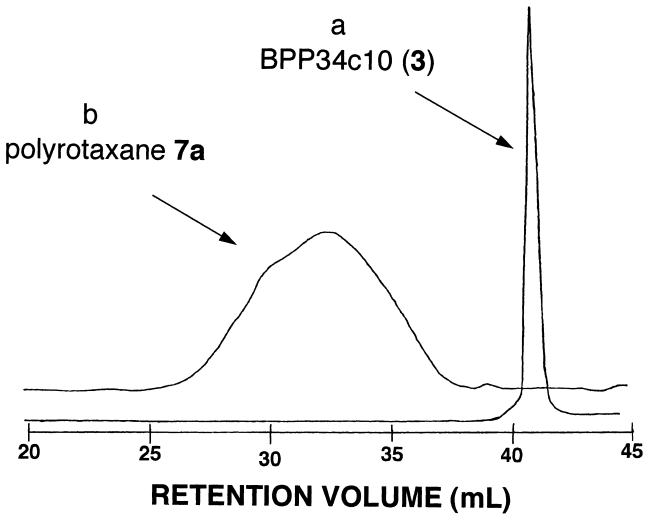


Fig. 4. GPC traces of (a) BPP34c10 (**3**), and (b) poly[(styrene)-*rotaxa*-(BPP34c10)] (**7a**, Sample E136-2, Table 1) in THF, UV detector.

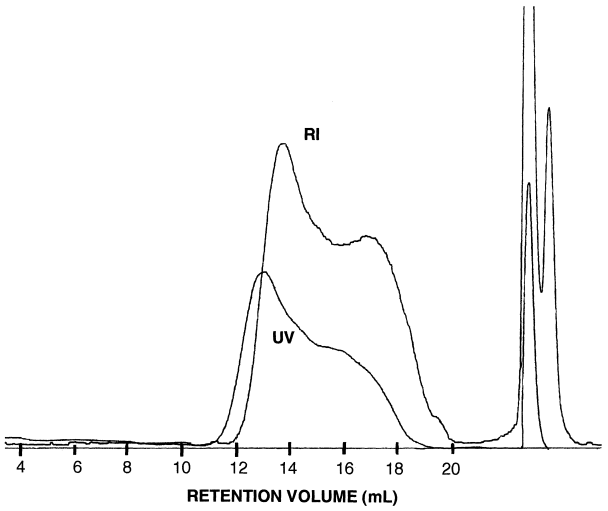


Fig. 5. GPC traces of poly[(styrene)-*rotaxa*-('42c14')] (**7c**, Sample L101-2, Table 1): in THF, refractive index and UV detectors.

of various samples with and without the crown ether present. For L261 versus L31-5 the conditions were virtually identical, but the apparent molecular weight of the polyrotaxane (L261) was higher than that of the polystyrene (L31-5). While the conditions were not exactly identical, comparison of E216-3 versus E216-4 shows the same trend; in sample E216-4, the higher concentration favored higher molecular weight, but this was not observed. A more subtle reason for these differences in molecular weights may be that the rate of termination relative to propagation is decreased in the case of the polyrotaxanes. It must be pointed out that we have no information on the distribution of crown ether units of the polyrotaxanes; it may be that threading promotes further threading and this would result in some chains having very low *m*/*n* values and others with high *m*/*n* values, rather than a uniform distribution.

3.1.2. Dispersion polymerization

To test the hypothesis that emulsions were the result of polyrotaxane formation, '42C14' was examined as a component of dispersion polymerizations. The crown ether was demonstrated to act as an emulsifier in dispersion polymerizations of styrene, presumably via polyrotaxane formation.

From Batches 1 and 2 in Table 2, it was found that 4,4′-azobis(4-cyanopentanoic acid) alone can not afford stable PS particles. When 18c6 (**6**) was used as an additive, no formation of stable PS micelles was observed. PEOs with low molecular weights could not produce stable emulsions; it was, however, found that PEO, M_n = 100 kg/mol did afford polymer particles to some extent, but they were not stable; they rapidly precipitated when the stirring was stopped. This suggested that chain transfer took place to a small extent.

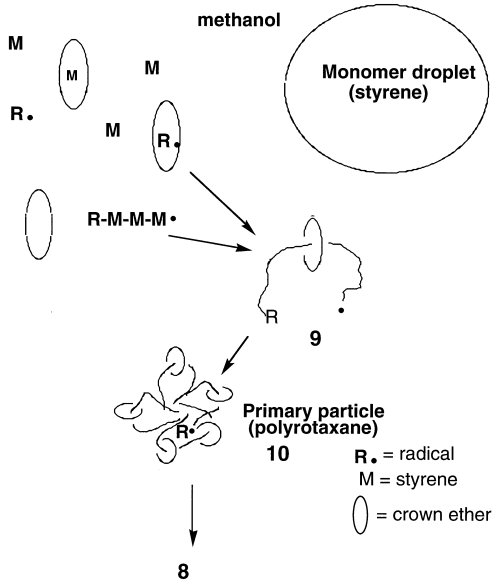
The formation of stable emulsions was achieved only with '42c14' (**5**) in either methanol or water with either AIBN or 4,4′-azobis(4-cyanopentanoic acid). This result

Table 2
Dispersion polymerization[a] of styrene using '42c14' (**5**) as a precursor to an in situ generated polyrotaxane surfactant

Batch	Initiator[b]	Additive (1.0 g)	Solvent (10 ml)	Emulsion[c]
1	A	—	Water	No
2	A	—	MeOH	No
3	A	18c6 (**6**)	MeOH	No
4	A	PEO(400)	MeOH	No
5	A	PEO(1500)	MeOH	No
6	A	PEO(3400)	MeOH	No
7	A	PEO(100 K)	MeOH	No[d]
8	A	'42c14' (**5**)	Water	Yes
9	A	'42c14' (**5**)	MeOH	Yes
10	B	'42c14' (**5**)	Water	Yes

[a]Reaction conditions: 1.5 g styrene, 1.5 mol% initiator, reflux (MeOH) or 70°C (water), 25 h.
[b]A: 4,4′-azobis(4-cyanopentanoic acid); B: AIBN.
[c]'No' means that the particles were unstable or coagulated upon polymerization; 'yes' means that the particles were stable (not precipitated within a week).
[d]Some particles were formed, but once stirring was stopped the particles precipitated within about 30 min.

strongly supports the importance of 'threading' for the formation of the emulsions. In fact it again rules out chain transfer as a possible mode of incorporation of the ethers; if this were the mechanism, then PEO and 18c6 would also function in the same manner. As described in Scheme 3, we propose that oligomeric growing polymer chains are threaded through the crown ether to give oligomeric, growing polypseudorotaxane radicals (**9**). Once the length of the growing chains reaches a certain critical value, they coagulate and precipitate to form a primary particle **10** which serves as a polymerization site as in a normal surfactant-free dispersion polymerization [55,56]. The threading 'anchors' the crown ether molecules so that they do not detach from the surface of the polymer particle **8** but act as permanent surfactant entities like a block copolymer [53] or non-ionic surfactant [57].



Scheme 3. Suggested mechanism of dispersion polymerization of styrene using '42c14' (**5**) to generate a polyrotaxane surfactant in situ.

3.2. Threading of preformed polystyrene

Threading of a preformed polyester ($M_n = 18.8$ kg/mol, PDI = 1.90) with **5** resulted in an m/n value of 2.0×10^{-2} [30]. Recently we found that a polyurethane effectively threaded through **5**, affording m/n values as high as 0.20, driven thermodynamically by hydrogen bonding [11]. An experiment of this type was also carried out with polystyrene, $M_n = 18.0$ kg/mol, PDI = 1.2, and **5** in THF. After purification using centrifugation as described above, NMR analysis indicated the sample had $m/n = 5 \times 10^{-4}$, i.e., it contained 0.3 mass% crown ether. Thus, as shown with the polyester this statistical threading methodology is not a very efficient way to prepare polyrotaxanes. Nonetheless, this

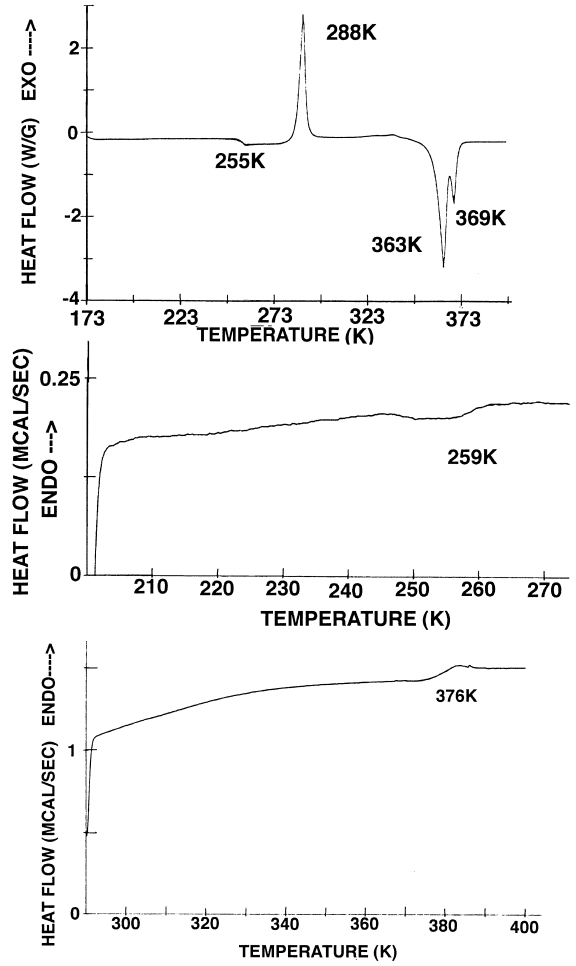


Fig. 6. DSC traces of (a) bis(*p*-phenylene)-34-crown-10 (**3**), second heating after quenching from the melt and (b) poly{(styrene)-*rotaxa*-[bis(*p*-phenylene)-34-crown-10]} (**7a**, Sample E136-1, Table 1, second heating). Heating rate: 10°C/min.

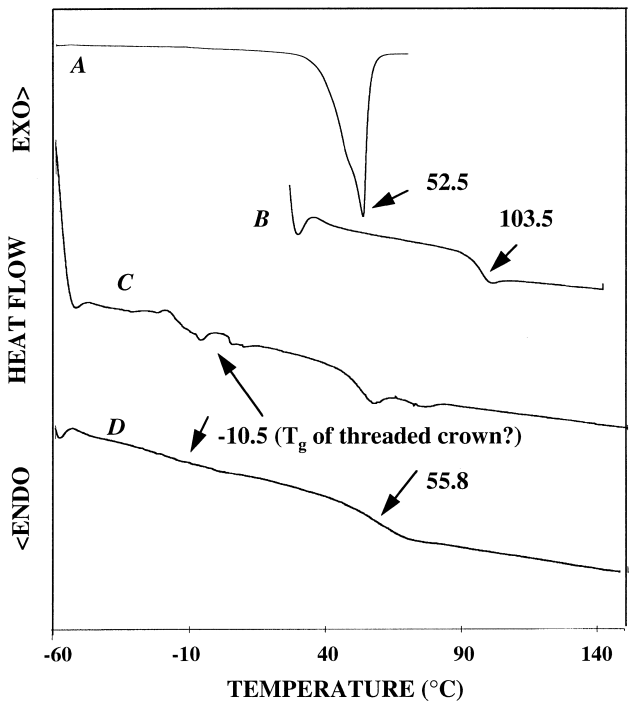


Fig. 7. DSC traces of (a) '42c14' (**5**, second heating), (b) PS ($M_n = 15.2$ kg/mol, third heat), (c) poly[(styrene)-*rotaxa*-('42c14')] (**7c**, Sample L261, Table 1, first heating) and (d) poly[(styrene)-*rotaxa*-('42c14')] (**7c**, Sample L261, second heating). Heating rate: 10°C/min.

polyrotaxane did form an emulsion in methanol, consistent with the mechanistic ideas of Scheme 3.

3.3. Thermal properties

The thermal behavior of the polyrotaxanes was investigated by DSC. Fig. 6 shows traces for BPP34c10 (**3**) and polyrotaxane **7a**, Sample E136-1. Fig. 7 shows the DSC traces of '42c14' (**5**), PS and **7c**, Sample L261. The polyrotaxanes did not show melting peaks for the crown ethers. The small extent of threading probably precludes crystallization of the threaded crown ethers, as we observed with poly(ester rotaxane)s [26,27]. Glass transitions of the polyrotaxanes were observed. For **7a** these were at − 14 and 103°C and for **7c** at − 10 and 56°C. The higher T_g is believed to be from the PS backbone and the lower one from the crown ether. Thus, the T_g of PS was decreased in the polyrotaxane as compared to homo-PS and the T_g of the crown ethers, which in free form is at − 18°C for **3** (Fig. 6; this compound is known to diplay two melting points because of dimorphism [49,50]) and at − 68°C for **5** [26], increased and broadened. The shift of T_g's can be understood as a result of some degree of phase mixing.

4. Conclusions

Free radical polymerizations of styrene in the presence of crown ethers afforded poly[(styrene)-*rotaxa*-(crown ether)]s **7**. The free radical polymerization with 30c10 (**4**) and BPP34c10 (**3**) did not give high loadings in **7a** and **7b**. However, with larger crown ether **5** polyrotaxanes **7c** with high threading yields (21–26 mass%) were synthesized, although fractionation probably contributed to the high values. The results show that in statistical threading the cavity size of the cyclic macromolecule is important to obtain high threading yields. The polyrotaxanes **7** showed surface active behavior due to the combination of two components with different solution properties (hydrophobic backbone–hydrophilic rings), like block copolymers. According to the DSC study the threaded structure of the polyrotaxane causes phase mixing to some extent on the basis of altered T_g's of the two components.

Acknowledgements

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